Enhanced Bioavailable Contaminant Stripping (EBCS): metal bioavailability for evaluation of phytoextraction success

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Abstract. Phytoextraction may be applied at field scale when the removal of bioavailable metals is the specific target of the technology. Residual metals in soil can be considered substantially inert or to be evaluated by site specific risk analysis.

Key words: phytoremediation, heavy metals, bioavailability, EBCS.

Introduction

Phytoextraction of metals: lights and shadows

The term phytoremediation identifies a set of technologies that employ plants for soil, sediment and contaminated water remediation. Due to their characteristics of simplicity, low costs and, above all, environmental benefits, phytotechnologies have raised considerable interest since the '90s in the context of *in situ* remediation techniques of contaminated soils.

Among the phytoremediation techniques, metals phytoextraction is, at least theoretically, a brilliant strategy of biological reclamation for non-biodegradable contaminants.

Phytoextraction and all the other phytotechnologies have been examined, discussed and applied, and the overall emerging framework has shown some positive results along with real limitations, that have highlighted the need for further efforts to make them more efficient. In fact, there is a remarkable gap between the number of the scientific papers based on laboratory tests and the results achieved in concrete actions for cleaning up. While the scientific community has found a challenging area of research, the field application of these technologies has met several difficulties that are often underestimated in the early stages of the theoretical study. The results from experiments conducted in hydroponics or in uncontaminated soils spiked with pollutants, although scientifically valid, do not reproduce the real conditions of contamination, causing a breach between the expectations resulting from the theoretical data and the practical realization of remediation. In many cases, moreover, it is impossible to predict the processes that affect the success of phytoremediation, such as those resulting from inadequate physical properties of soil..

The bioavailability of contaminants: an undervalued aspect.

The evaluation of contaminant bioavailability is essential for the appropriate application of the technology. In soil, the bioavailability is the resultant of complex mechanisms of mass transfer and absorption, which are affected by the contaminant properties, the chemical and physical characteristics of soil and the biology of organisms involved. The transfer of heavy metals from the solid phase into the soil solution is fundamental. Only after being released in the aqueous phase a contaminant can move freely towards the plant roots and be absorbed. Thus, the metal speciation in soil becomes critical for the phytoextraction potential testing under field conditions, while the concentration in the liquid phase is an essential parameter for the final success of remediation (Petruzzeli and Pedron, 2006). In particular, it is noteworthy that in soils characterized by high contents of humic acids or by a significant presence of clays, metals show strong bonds with these components that can heavily reduce the

phytoextraction process. It has also been observed that stronger bonds correspond to the increasing time of residence of metals in soil and therefore a decrease in the efficiency of phytoextraction.

In a recent study conducted in England on soil contaminated by arsenic (As), a simplified modeling analysis was developed to evaluate the possible use of the fern *Pteris vittata* in remediation by phytoextraction (Shelmerdine et al., 2009). This study shows that the amount of metals undergoing a process of phytoextraction can be correlated with the amount present in the soil solution. Assuming that the arsenate ions are the only species present in the liquid phase, the quantity absorbed by the plant can be expressed by the relation:

$$As\ (_{Veg}) = k_1\ (H_2AsO^-) / 1 + k_2\ (H_2AsO_4) + k_3\ (HAsO_4^{2-}) / 1 + k_4\ (HAsO_4^{2-}) \qquad (1)$$

where: k_2 and k_4 are the constants that describe the absorption reaction of the two arsenate ions on the available radical sites; k_1 and k_3 are terms which include the constants of the above reaction, the transfer coefficients from the roots to the aerial part of plants and the density of adsorption sites on the roots. This model is based on some simplifications, including the assumption that: i) the ratio between the contaminant concentration in the root system and that in the apical part remains the same during the plant growth; ii) the concentration of arsenate in the soil solution close to the roots is constant; iii) arsenate is the only As species absorbed by plants. However, the proposed model may be integrated with a solubility model in which the amount of arsenic in the soil solution is described by the distribution coefficient Kd, defined by the ratio of As ion concentration between the solid and the liquid phases. Kd values depend on soil pH according to the relationship:

$$\log_{10} Kd = a + b\ pH \qquad (2)$$

where the constants a and b derive from the specific chemical-physical characteristics of the polluted soil considered.

The combination of the two equations allows to predict the amount of arsenic that may be removed for each harvest :

$$As_{soil}\ (t+1) = Soil_{As}\ (t) - (As_{Veg}\ W_{Veg} / W_s) \qquad (3)$$

where As_{Suolo} is the total concentration in soil at various times (t, t +1, etc. ..), As_{Veg} is the metal concentration in the plant (mg kg^{-1}), W_{veg} is the aerial biomass of the plant removed at each harvest (t ha^{-1}) and W_s is the weight of the soil layer affected (t ha^{-1}).

The described model, applied to soils historically contaminated by arsenic, identifies an extreme variability in the amount of metal that can be removed by a phytoextraction process. This amount is closely related to the specific characteristics of soils, especially to those parameters that determine the bioavailable fraction of metal. The methodological approach reported for arsenic can be applied to other inorganic contaminants. The uptake of As by plants increases with increasing pH from 6.0 up to approximately 8-8.5, while for metals such as Zn, Pb and Hg the absorption is favored at acidic conditions, with pH values ranging between 4.5 and 6.0.

These models make it possible to predict the time necessary to achieve the aims of remediation, even though the final verification is often hampered by the extreme heterogeneity of the contaminated soils. The great difference among soils makes it difficult, if not impossible, to obtain reliable mass balances, thus the equation (3) encounters objective difficulties of application in the passage from a theoretical phase of modeling to the practical implementation of the technology.

New prospects of phytoextraction

Both the theoretical modeling and the considerations deriving from the cases of application on a real scale show that a natural limit of phytoremediation is represented by the considerably long time requested, since it is a technique related to the cycles of growth of plants. Recovery times of decades are realistic in many scenarios, and this inevitably reduces the attractiveness of phytoremediation, especially if rapid results and a total removal of pollutants are required.

In order to increase the efficiency of phytoextraction, fertilizers can be used to enhance the productivity of selected plants. Ammendants, such as organic acids or synthetic chelators, can be added to soil in order to facilitate the desorption of metals from the solid phase and to increase, consequently, their solubility (assisted phytoextraction). Other promising possibilities consist in enriching the rhizosphere of plants with rhizobacteria that promote growth, or in employing plants characterized by a higher productivity and a higher transpiration power than the hyperaccumulator species. Genetic engineering, finally, has made it possible to increase the tolerance and the accumulation of metals in the species already characterized by a high production of biomass. In the case of heavy metal pollution, the application of phytoremediation on a large scale presents some problems and, in most cases, excellent results have not yet been achieved. With the aim of optimize the technique, the research is moving in different directions. The use of genetically-modified plants seems to offer important perspectives, including economic benefits, and the addition of new agents mobilizing metals to soil appears to increase the bioavailable amount without creating undesirable environmental side-effects (Doumett et al., 2011). A third possibility is represented by the selection of a technology that a decade ago was defined Bioavailable Contaminant Stripping (BCS) (Hamon and McLaughlin 1999). It originates from the intrinsic properties of the method, whose applicability has always been linked to the bioavailability of heavy metals. The

phytoextraction acts, in fact, only on the amounts of metals that are, or may be, bioavailable, as shown in equation (1), specifically for arsenic. Nevertheless, most contaminated sites contain a residual fraction of metal which is bound in an irreversible manner to soil surfaces and that phytoextraction cannot remove. The BCS may give new perspectives to the use of phytoremediation, as it considers only the bioavailable fraction of metals consequently resulting in a significant reduction of reclamation time.The only uncertainty of BCS method is determined by the lack of knowledge concerning the time necessary to the reintegration of mobile metals in the soil solution, once the original soluble amount has been entirely or in part removed by plants. This problem can be overcome through the use of a mobilizing agent capable of rapidly solubilizing the maximum possible amount of a metal, in order to simulate the slow release process of metallic elements from the soil solid phase, similarly to what occurs during the process of assisted phytoextraction. Thus, the amount of mobilized metal correspond to the maximum potentially available, and it can be removed by plants in one or more cycles of growth (Enhanced Bioavailable Contaminant Stripping or EBCS).

Finally the EBCS approach shown in Figure 1 is divided into four phases: 1. Evaluation of the metal in a potentially bioavailable form. Soluble or easily dissolved amounts are determined (i.e. the exchangeable species). 2. Determination of the total amount of long term extractable metal with time. This step is performed making use of metal mobilizing agent. Since the action of mobilizing agent is much greater than any natural process, the amount determined in this step can be considered (based on a precautionary approach) the maximum quantity of metal available to plants, and may be used to define the clean-up target. 3. Growth of plants under greenhouse, in order to select the most efficient species on the basis of their ability to take up both the original and the newly created available fractions which are brought into solution by the specific mobilizing agent. Control of the possible presence of metals in the leachate of the mesocosms. 4. After harvesting, further cycles of plant growth are performed on the same soils, in order to control the absence of residual metal in bioavailable forms. In parallel, an extraction with mild agents is conducted to check the absence of mobile chemical forms of the metallic element. When the metal concentration in plant is negligible and no amount of metal can be extracted from soil, the residual concentration of metal can be considered safe.

Conclusion

Since the early '90s the concept of soil quality has evolved in response to the increased demand for a sustainable land use. It has been recognized that soil is essential for the environment. The European Community has drafted documents to support a strategy for soil protection. In particular, among the major threats to soil, contamination is one of the most important.

In remediation procedures soil quality has often been considered only marginally, without paying enough attention to the possible implications that the technologies employed may have on soil.

Phytoremediation, which can improve soil quality, can bring new perspectives if evaluated to reduce the mobile and bioavailable fractions through plants uptake, since the bioavailable metals can enter the environmental processes, and thus be a real danger. This strategy should be carefully checked using an appropriate risk analysis to assess the potential risks arising from the presence of any residual quantity of metals, even if inert, in a contaminated site.
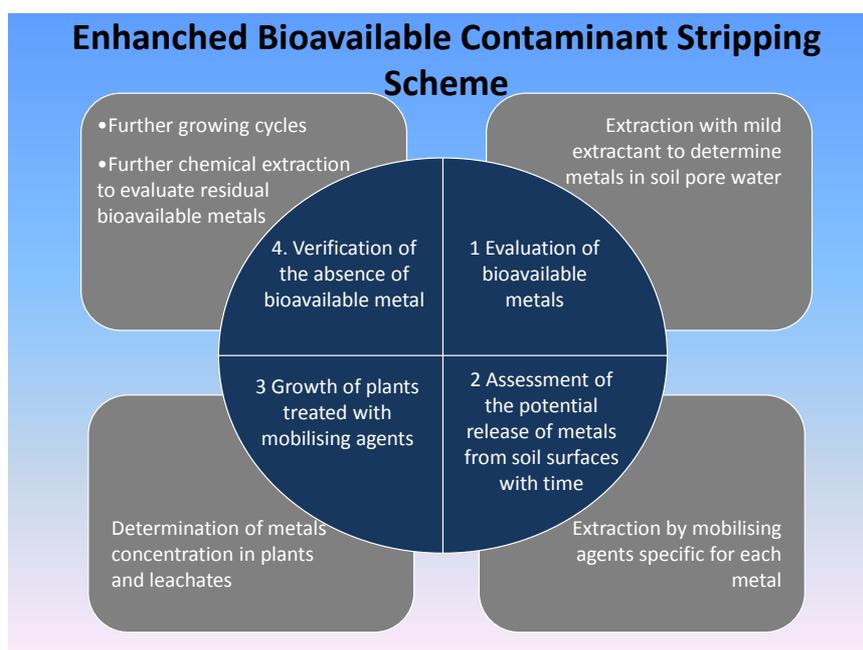

Fig. 1. Scheme of EBCS approach.

Acknowledgements

References

Doumett S., Fibbi D., Azzarello E., Mancuso S., Mugnai S., Petruzzelli G., Del Bubba M. Influenceof the application renewal of glutamate and tartrate on Cd, Cu, Pb and Zn distribution between contaminated soil and *Paulownia Tomentos*a in a pilot- scale assisted phytoremediation study. Int. J. Phytoremediation 2011; 13: 1-17.

Hamon R. E., McLaughlin M. J. Use of the hyperaccumulator *Thlaspi cearulescens* for bioavailable contaminant stripping. In: Wenzel W. W., Adriano D. C., Alloway B., Doner H., Keller C., Lepp N.W., Mench M., Naidu R., Pierzynski G. M. (Eds.), Extended Abstracts of the Fifth International Conference on the Biogeochemistry of Trace Elements (ICOBTE), 1999. Vienna, 908-909.

Petruzzelli G., Pedron F. "Bioavailability" at heavy metal contaminated sites: a tool to select remediation strategies", in International conference on the remediation of polluted sites (BOSICON), 2006. Roma, 1-8.

Shelmerdine P.,,Black, C., McGrath S., Young S. Modelling phytoremediation by the hyperaccumulating fern, *Pteris vittata*, of soils historically contaminated with arsenic. Env. Poll. 2009; 157:1589-1596.